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**Observation of the Photorefractive Effect in a Polymer**

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## OBSERVATION OF THE PHOTOREFRACTIVE EFFECT IN A POLYMER

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**ABSTRACT:** We report the first observation of the photorefractive effect in an amorphous electro-optic material, the nonlinear optical polymer bisphenol A diglycidylether 4-nitro-1,2,phenylenediamine (BisA-NPDA) made photoconductive by doping with the hole transport agent diethylaminobenzaldehyde-diphenyl hydrazone (DEH). The gratings formed exhibit: dynamic writing and erasure, strong electric field dependence, polarization anisotropy, diffraction efficiencies up to  $6 \times 10^{-3}$  in a 356  $\mu\text{m}$  film, and estimated photorefractive space-charge fields up to 45 kV/cm at an applied field of 126 kV/cm. Continuous realignment of the nonlinear molecules in the polymer permits external control of grating readout independent of the space-charge field formed.

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The photorefractive effect remains a laboratory curiosity "on the verge of exploitation," more than twenty years after its accidental discovery and the early realization of its potential applications.<sup>1</sup> Among the many photorefractive applications which have been proposed are:<sup>2</sup> high density optical data storage; a wide range of image processing techniques; phase conjugation; simulations of neural networks and associative memories; optical switching; optical computing; and programmable interconnection. But, despite what it *can* do, there is as yet little that the photorefractive (PR) effect *does* do that is competitive with existing devices. One of the primary roadblocks has been the fact that the materials which have exhibited the effect (until recently,<sup>3</sup> only inorganic crystals) tend to be difficult and expensive to make and prepare. The purpose of this report is to describe the first of an entirely new class of easily fabricated PR materials, doped nonlinear optical polymers.

The PR effect begins with the redistribution and trapping of charge in the bulk of a photoconducting insulator or semiconductor under nonuniform illumination. The electric fields associated with the trapped charge alter the index of refraction of the material through the electro-optic (EO) effect, thus producing a phase replica, or hologram, of the optical intensity distribution. The ingredients necessary for producing a PR phase hologram are therefore: photoionizable charge generator, transporting medium, trapping sites, and second-order nonlinearity.

We have made a polymeric PR material, the first to our knowledge, to take advantage of the relative ease of fabrication and processing and of the large EO response attainable

with a low dielectric constant in organic materials.<sup>4</sup> Polymers have been separately made electro-optic by poling guest or attached nonlinear chromophores<sup>5, 6</sup> and made photoconducting at virtually any wavelength by doping with charge generation and transporting agents.<sup>7, 8</sup> In this work, the EO material is the epoxy prepolymer bisA-NPDA composed of bisphenol A diglycidylether (bis A) reacted with the nonlinear chromophore 4-nitro-1,2,phenylenediamine (NPDA) which has been studied previously in its crosslinked form as a stable second order material.<sup>9</sup> The prepolymer had a glass transition temperature  $T_g = 65^\circ$  and number average  $\overline{M}_n = 2200$  and weight average  $\overline{M}_w = 6900$ , molecular weights. Though the molecular weights remained low and little additional crosslinking occurred in subsequent preparation and measurements, the term 'polymer' will henceforth be used to in preference to 'prepolymer'. The bisA-NPDA polymer provides second-order nonlinearity when the NPDA chromophores are oriented in an electric field. It will be shown below that the NPDA also provides optical absorption for the charge generation process.

Monopolar charge transport is facilitated by addition of the hole transport agent, diethylaminobenzaldehyde-diphenyl hydrazone (DEH), to the polymer to form connected pathways for the hopping motion of holes as is done in the charge transport layer of electrophotographic photoconductors.<sup>8</sup> In molecularly doped polymers, trapping centers are invariably present due to defect and conformational disorder inherently present in the amorphous structure. Therefore, for these initial studies, no additional traps were added.

The polymer and DEH were codissolved in the appropriate ratio in PM (propylene glycolmonomethyl ether) or PM acetate, stirred thoroughly, and filtered. Samples were made by dripping 1-3 ml of the polymer DEH-solvent mixture onto two ITO-coated glass plates

set on a hot plate. The mixture was dried at 95° C for 30 minutes to remove most of the solvent and then the two plates were pressed together face-to-face and quenched to room temperature to form a plate-polymer-plate sandwich. Slight cross-linking of the polymer was evident after this brief exposure to high temperature. Numerous samples 178  $\mu\text{m}$  to 533  $\mu\text{m}$  thick prepared in the same manner exhibited similar EO, photocurrent, and PR properties.

The separate contributions that the host polymer and the hole transport agent make to the photoconductivity are illustrated in Fig. 1. The absorbance of the sample in the red (left scale) is not significantly different from the undoped polymer since DEH absorbs in the blue. The strong absorption onset is due to the first electronic transition of the NPDA. The inset to Fig. 1 shows that the photosensitivity  $\sigma_{\text{pc}}/I$  (photoconductivity per unit intensity) increases rapidly once sufficient DEH is added, consistent with the establishment of a conductive network for charge transport. The measured photocurrents were approximately linear in the bias voltage and in intensity and were determined to be free from significant contributions due to heating. The photosensitivity of a sample (slightly more than a week old) made with 30 wt.% DEH has a spectral dependence which closely follows the measured optical absorbance of the sample (Fig. 1, right scale). However, the photosensitivity does not decrease nearly as rapidly as the absorbance beyond 650 nm, perhaps due to additional photogeneration at NPDA-DEH charge transfer pairs.

The photoconductivity of samples stored at room temperature in the dark was observed to decay with a 50 % lifetime of one week, likely due to slow aggregation of the DEH in the polymer. A sample stored at 7 °C decayed much more slowly, with a 50 % lifetime exceeding two months.

Usually, epoxy polymers are aligned by poling and then crosslinked at elevated temperatures to produce stable nonlinearity.<sup>9</sup> Attempts to cross-link our samples produced a loss of optical quality perhaps due to decreasing solubility of the DEH in the cross-linked regions. Hence we chose to not cross-link, to align at room temperature, and to perform most experiments with a dc electric field present both to permit additional control of the holographic readout and to simplify sample preparation. Electrode poling of the samples is possible at room temperature because the polymer is softened by mixing with DEH (as confirmed by differential scanning calorimetry). Therefore the EO response can be readily controlled using a bias voltage, a property which may be useful for new applications.

Using a Mach-Zehnder interferometer to measure EO phase changes at low (10 - 10,000 Hz) frequencies,<sup>10</sup> we observed that the (steady-state) EO coefficient is proportional to the magnitude of the applied field except for a small residual hysteretic alignment retained in the absence of the applied field. Upon changing or reversing the applied dc field, the observed EO coefficient rises in a matter of minutes to approximately 90% of its long-time (i.e. many hours) value. The left-hand scale of Figure 2 shows the variation of the square of the effective (steady-state) EO coefficient (times the cube of the index of refraction, which does not change significantly in an electric field) of a 356  $\mu\text{m}$  thick 30 wt. % DEH mixture for p-polarized 632.8 nm radiation incident at an external angle of 60°. At this angle and polarization, the effective EO coefficient (neglecting birefringence)  $r_{\text{eff}} = r_{33} \sin^2\alpha + r_{13} \cos^2\alpha$  is a linear combination of the longitudinal  $r_{33}$  and transverse  $r_{13} = r_{23}$  coefficients where the

3-direction is the direction of the applied electric field which is normal to the plane of the film and  $\alpha = 30.6^\circ$  (for  $n = 1.7$ ) is the angle of propagation within the film. The sign of  $r_{eff}$  is positive with respect to the direction of the applied electric field.

Thus, three of four necessary ingredients for a PR material, absorption, transport, and EO response, can be easily measured in our polymer mixtures. The polymer would be expected to supply a large density of traps, which may be polymer chain ends or other defects, but there is no guarantee that these traps will be properly compensated and photoionizable as required for the production of an erasable PR space-charge field.<sup>2</sup> The presence of the PR effect and therefore a sufficient number of useful traps has been verified in the polymer films by volume holography in which two mutually coherent Gaussian 'writing' beams at a wavelength of 647.1 nm and with equal intensities of 13 W/cm<sup>2</sup> were intersected at the sample at incidence angles of 30° and 60° (in air), respectively, thus producing interference fringes with 0.2  $\mu$ m spacing oriented 24° from the film plane. A third, much weaker, 'reading' beam directed opposite to the 60° writing beam was Bragg diffracted from the holographic grating created in the polymer by the writing beams. The diffraction efficiency was recorded as the ratio of the diffracted power to the incident reading beam power. The writing beams could be either s- or p-polarized, but only a p-polarized reading beam produced measurable diffracted signal, also with p-polarization. This anisotropy is consistent with the expected anisotropy of the EO coefficient.

The influence of the externally applied electric field on diffraction efficiency is shown in Fig. 2. The diffraction efficiency  $\eta = (n^2 r_{eff} \pi L G E_{sc} / 2\lambda)^2$  increases rapidly with the applied electric field through increases in both the PR space-charge field  $E_{sc}$  and the EO response



$n^2 r_{\text{eff}}$ , where the interaction length  $L = 391 \mu\text{m}$  is slightly larger than the polymer film thickness at the oblique angle of propagation,  $\lambda = 647.1 \text{ nm}$ , and  $G$  is a polarization and geometrical factor equal to 0.45. The PR space-charge field in the standard model for the PR effect is<sup>2, 11</sup>

$$E_{\text{sc}}^2 = \frac{E_d^2 + E_0^2}{(1 + \Lambda)^2 + \Lambda^2 (E_0/E_d)^2}, \quad (1)$$

where  $E_0$  is the component of the applied electric field along the grating wavevector,  $E_d = k_x k_B T / e = 1.29 \text{ kV/cm}$  and  $k_x = 2\pi n / (\text{grating spacing}) = 5 \times 10^5 \text{ cm}^{-1}$ . The inset to Fig. 2 shows  $\eta$  divided by  $n^2 r_{\text{eff}}$ , which should be proportional to  $E_{\text{sc}}^2$ . The solid line is a least-squares fit to Eq. 1 with two adjustable parameters: a prefactor which takes into account the uncertainty in knowing the precise EO coefficient at the grating location<sup>12</sup> and  $\Lambda = 0.018$  which yields the effective density of photorefractive traps  $N_{\text{pr}} = k_x^2 \epsilon \epsilon_0 k_B T / \Lambda e^2 = 5.7 \times 10^{17} \text{ cm}^{-3}$  ( $\epsilon = 2.9$ ). The maximum  $E_{\text{sc}}$  reached, at an applied field of 126 kV/cm, from Eq. 1 is 45 kV/cm, a value which is much larger than obtained in inorganic PR materials due presumably to the low dielectric constant of the organic polymer.<sup>17</sup>

To further establish that the observed gratings, once established, were indeed electro-optic in origin, we recorded gratings at large applied voltage, removed the writing beams, and observed the diffracted signal as the applied voltage was altered, with typical results shown in Fig. 3. The grating was recorded with a bias voltage of -3000 V (a field of -84.3 kV/cm with respect to an arbitrary absolute choice of polarity) for 2.5 minutes. (The fluctuations in the signal as it rises to its steady-state value are due to slow changes in the optical paths of the writing beams.) At b, both writing beams were switched off as was the applied voltage;

the signal rapidly decreased due to the rapid relaxation of the alignment of the nonlinear chromophores. However, the built-up space-charge remained (except for the slow erasure by the much weaker reading beam) as was confirmed by the return of the diffracted signal upon application of a positive voltage at c, thus aligning the nonlinear molecules opposite to their original orientation. At d, the voltage was again reversed, slowly reversing the orientation of the nonlinear molecules and restoring the diffracted signal. (The signal did not recover all of its initial magnitude between c and e due to the slow decay of the space-charge field and the sluggishness of the molecule alignment.) At e, one of the writing beams was turned back on to erase the space-charge field. Thus, Fig. 3 establishes the relative independence of the space-charge field formation and erasure from the molecular alignment whose only purpose is to permit readout. This is in sharp contrast to the situation in crystalline PR materials (with the exception of a paraelectric material such as PLZT<sup>13</sup>) in which the EO response is permanent.

The holographic gratings could be repeatedly written and erased dozens of times without noticeable degradation. The need for large external electric fields during grating recording can be understood, not because of the EO alignment which could readily be produced after the space-charge pattern had been established, but because an applied field is necessary to separate the photogenerated charges. As Eq. 1 shows, in the absence of an applied field, the steady-state space-charge field is equal to  $E_d = 1.29 \text{ kV/cm}$  which would yield a diffraction efficiency  $2 \times 10^{-3}$  in our samples even with a readout field of  $126 \text{ kV/cm}$ . As an additional test, we recorded gratings in the absence of an applied field and, after blocking the writing beams so that the space-charge would remain fixed, applied a large external electric field.

No signal was observed larger than the approximately  $1 - 5 \times 10^{-8}$  background scatter from inhomogeneities in the sample.

The time constant of growth or decay of PR gratings is proportional to the photoconductivity. To test this in our samples, we measured the (light-induced) erasure rate of the holographic gratings and the photoconductivity of the same polymer film. The bias field was kept constant during recording and erasure. The holographic speed and the photoconductivity both monotonically increased with increasing applied electric field, doubling at approximately 100 kV/cm, with a maximum erasure rate at 13 W/cm<sup>2</sup> of 0.065 s<sup>-1</sup>. Field dependence of the photoconductivity is not uncommon in organic photoconductors due to the pronounced dependence of the photogeneration rate<sup>14</sup> and the mobility<sup>15</sup> on the electric field. The dark storage time (i.e., the lifetime of the space-charge field with all optical beams blocked) was 500 seconds with no clear dependence on the applied electric field.

The PR effect has a number of unique features which distinguish it from any other known mechanism of grating formation. The clearest single signature of PR gratings, dynamic two-beam energy coupling,<sup>16</sup> an exchange of intensity between two beams interacting via a mutual photorefractive grating, has not yet been observed in our polymers because of the low diffraction efficiencies achieved. However, the electric field dependence of the grating formation and read-out, the correlation with photoconductivity and EO response, and the cyclic erasability eliminate the possibility that the observed effect is due to any mechanism other than photorefraction, such as photochromism, photochemistry or photophysical changes in molecular structure. Hence, the observations detailed in this letter, taken together,

provide unequivocal evidence that the molecularly doped polymer systems studied are indeed photorefractive.

#### **ACKNOWLEDGEMENTS**

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12. Though both the EO and grating measurements of Fig. 2 were made on the same sample, they were made at different locations; a sampling of 36 separate spots 40  $\mu\text{m}$  in diameter over a 4 mm<sup>2</sup> area yielded a range of EO coefficients with a standard

deviation of 12 % and a maximum deviation of 25 % from the mean. Also, the EO coefficient of the polymer was approximately 10 % higher at 632.8 nm than at 647.1 nm and separate measurement revealed that the piezoelectric coefficient  $d_{33} \sim +0.2$  pm/V, which may contain a contribution from electrode attraction, also made a significant (10-30 %) contribution to the observed EO measurements. The data in Fig. 2 are uncorrected for these observations.

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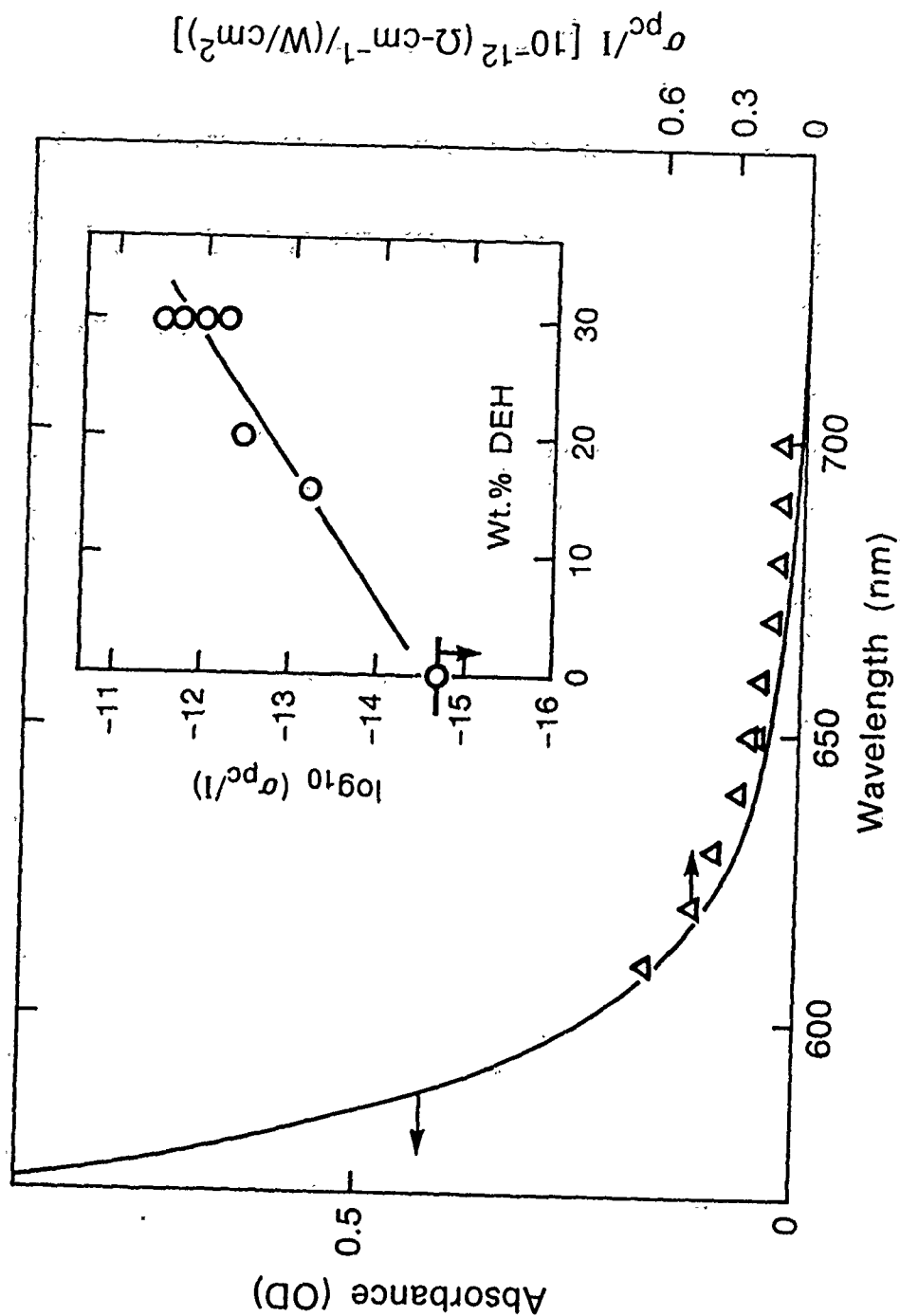


Fig. 1. Absorption (left ordinate) and photosensitivity (right ordinate) of the BisA-NPDA polymer mixed with 30 wt. % DEH. The inset shows the photosensitivity (measured at with 647.1 nm, 1.4 W/cm<sup>2</sup> illumination, 28 kV/cm field) of the polymer mixed with increasing concentrations of DEH. (The point at 0 wt. % is an upper limit only.)

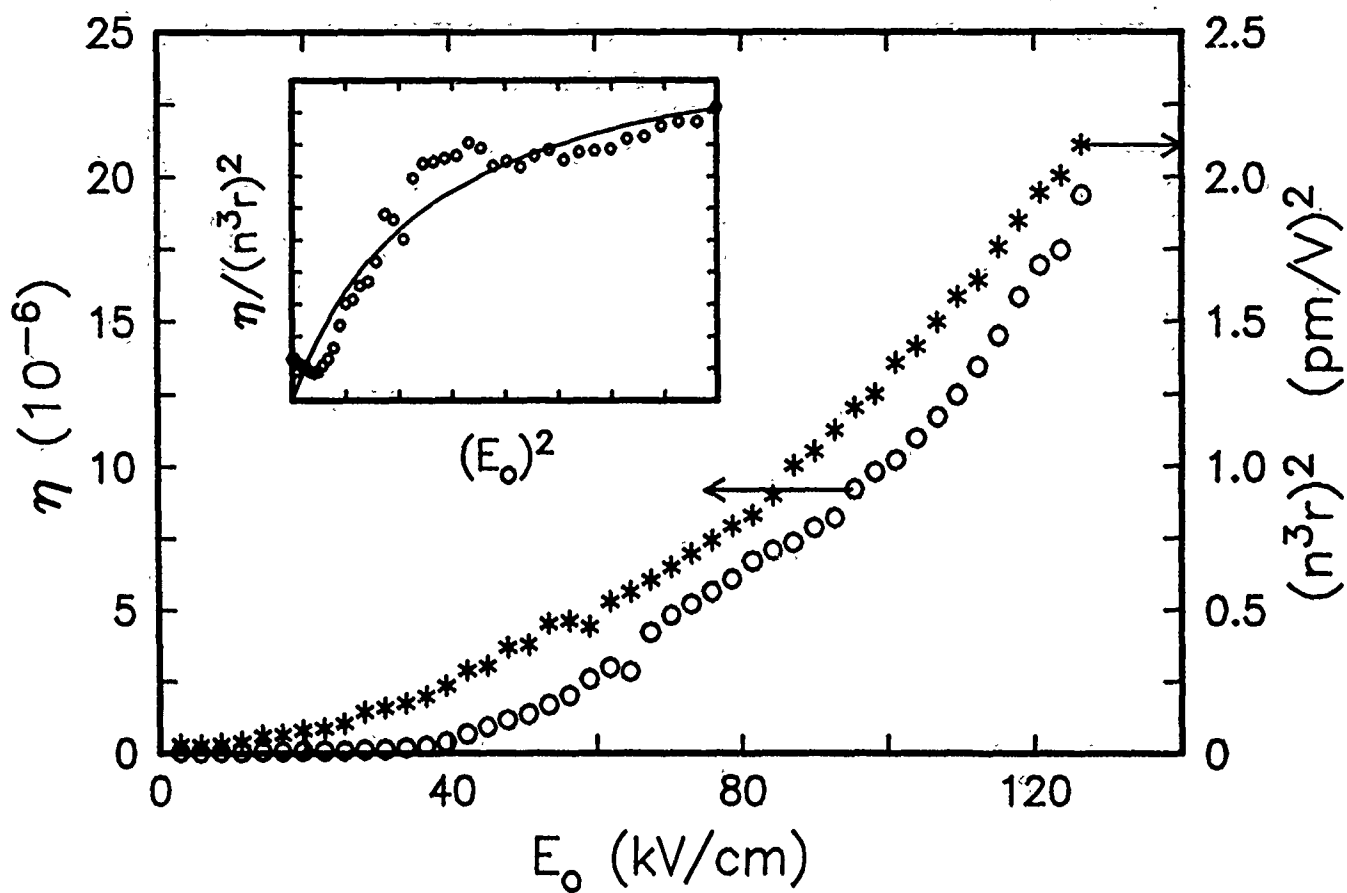


Fig. 2. Electro-optic coefficient (at 632.8 nm) and diffraction efficiency (at 647.1 nm) of a 356  $\mu\text{m}$  thick film of the polymer mixture BisA-NPDA:DEH (30 wt. %).



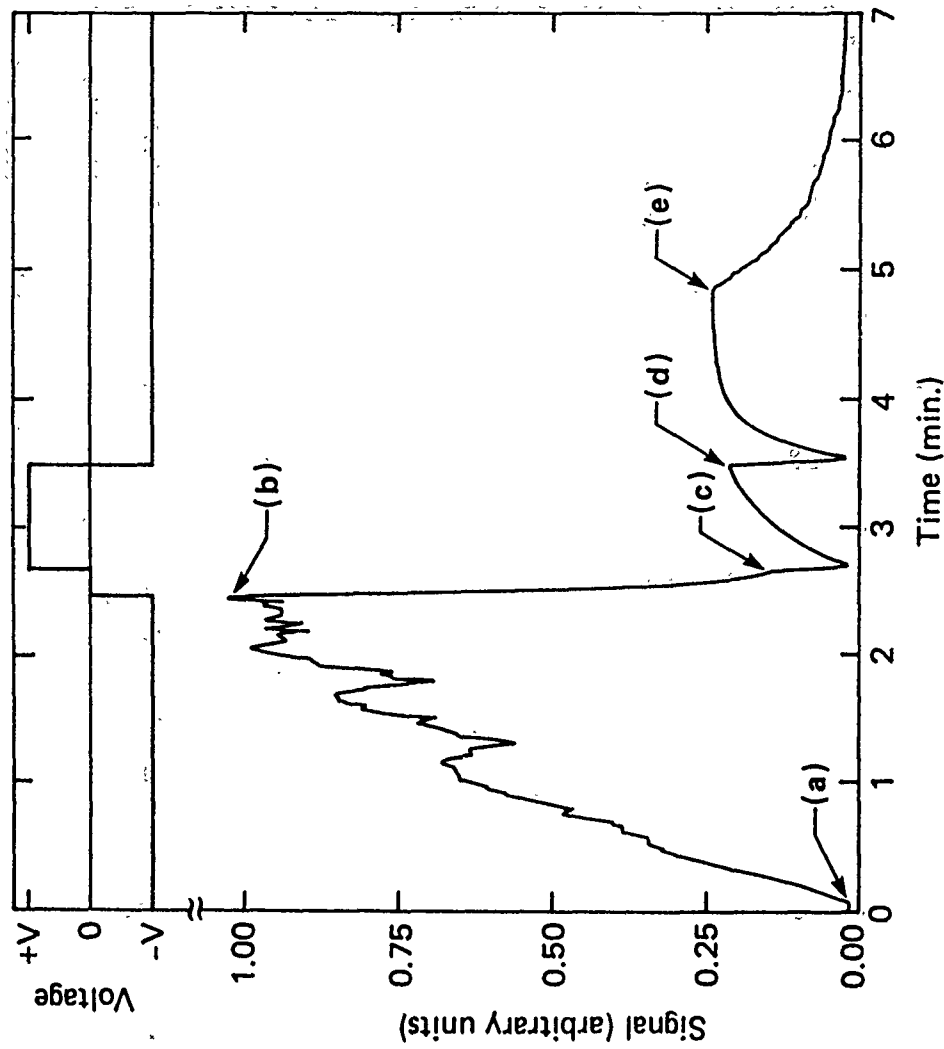


Fig. 3. Effect of applied electric field on grating readout by a weak reading beam: a-b) writing the grating in the presence of a negative voltage; b-c) writing beams and applied voltage turned off; c-d) positive voltage applied; d-e) negative voltage applied; e+ ) grating erasure by one strong beam.

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